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Docket No.: M0925.70086US00

(PATENT)

### N THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:

Timothy M. Swager

Serial No.:

09/777,725

Confirmation No.:

6084

Issued:

March 6, 2007

Patent No.:

7,186,355

For:

INSULATED NANOSCOPIC PATHWAYS, COMPOSITIONS AND

DEVICES OF THE SAME

Examiner:

J. Riley

Art Unit:

1637

Certificate of Mailing Under 37 CFR 1.8(a)

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being deposited with the U.S. Postal Service on the date shown below with sufficient postage as First Class Mail, in an envelope addressed to: Attention: Certificate of Correction Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Dated: January 18. 2008

Tina M. Hanifin

### TRANSMITTAL LETTER

Attention: Certificate of Correction Branch

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Dear Sir:

Enclosed are the following items for filing in connection with the above-referenced

#### Patent:

- 1. Request for Certificate of Correction;
- 2. Certificate of Correction; and
- 3. Return Receipt Postcard.



Application No.: 09/777,725

U.S. Patent No.: 7,186,355

Docket No.: M0925.70086US00

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to

be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 23/2825, under Docket No.

2

M0925.70086US00. A duplicate copy of this paper is enclosed.

Dated: January 18, 2008

Respectfully submitted

Timothy J. Oyer, Ph

Registration No.: 36 628 Karen V. Martin, Ph.D.

Registration No.: 61,652

WOLF, GREENFIELD & SACKS, P.C.

Federal Reserve Plaza 600 Atlantic Avenue

Boston, Massachusetts 02210-2206

(617) 646-8000



Docket No.: M0925.70086US00

(PATENT)

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Patent:

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Application No.: 09/777,725 2 Docket No.: M0925.70086US00

U.S. Patent No.: 7,186,355

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 23/2825, under Docket No. M0925.70086US00. A duplicate copy of this paper is enclosed.

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Docket No.: M0925.70086US00

(PATENT)

### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:

Timothy M. Swager

Serial No.:

09/777,725

Confirmation No.:

6084

Filed:

February 5, 2001

Patent No.:

7,186,355

For:

INSULATED NANOSCOPIC PATHWAYS, COMPOSITIONS AND

**DEVICES OF THE SAME** 

Examiner:

J. Riley

Art Unit:

1637

Certificate of Mailing Under 37 CFR 1.8(a)

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being deposited with the U.S. Postal Service on the date shown below with sufficient postage as First Class Mail, in an envelope addressed to: Attention: Certificate of Correction Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Dated: January 18, 2008

## REQUEST FOR CERTIFICATE OF CORRECTION PURSUANT TO 37 CFR 1.322

Attention: Certificate of Correction Branch

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Dear Sir:

corrected.

Upon reviewing the above-identified patent, Patentee noted errors which should be

In the Specification:

At column 1, line 10, please insert the following:

-- Statement Regarding Federally Sponsored Research or Development

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1315443.1

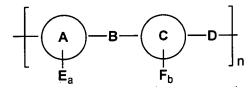
Patent No.: 7,186,355

This invention was made with the support under the following government contract: N00014-97-1-0174 awarded by the Office of Naval Research. The government has certain rights in the invention.--

2

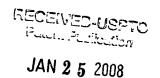
At column 8, line 27, please insert the following:

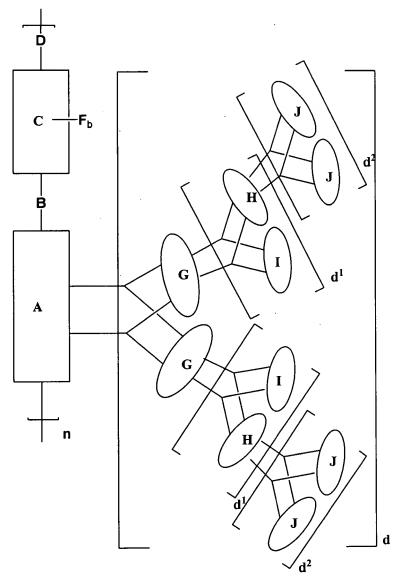
--In some embodiments, an article of the present invention may comprise a nanoscopic pathway having a conductivity, an insulating dielectric surrounding the nanoscopic pathway, and a nanoscopic switch in electronic communication with the nanoscopic pathway being capable of altering the conductivity of the nanoscopic pathway. The nanoscopic pathway may comprise a conducting polymer, wherein the conducting polymer has a structure comprising the formula:



wherein A and C are aromatic groups; B and D can be a heteroatom or metal and chosen from a group of N, P, S, As, Se, or -CC-M-CC-(M=FeL<sub>x</sub>, RuL<sub>x</sub>, PdL<sub>x</sub>, PtL<sub>x</sub>, CoL<sub>x</sub>, RhL<sub>x</sub>, where L is neutral (phosphine, nitrogen, or  $\pi$ -arene based ligand) or charged (nitrogen, oxygen, or charged  $\pi$ -arene ligand), or are selected from the group consisting of a carbon-carbon double bond and a carbon-carbon triple bond; and any hydrogen on aromatic group A and C can be replaced by E and F respectively, wherein a and b are integers which can be the same or different and a = 0 - 4, b = 0 - 4 such that when a = 0, b is nonzero and when b = 0, a is nonzero, and at least one of E and F includes a bicyclic ring system having aromatic or non-aromatic groups optionally interrupted by O, S, NR<sup>1</sup> and CR<sup>1</sup><sub>2</sub> wherein R<sup>1</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy and aryl and n is less than about 10,000, and wherein, when E or F is not said bicyclic ring system, E or F is a part of aromatic group A or C.

In some cases, E<sub>a</sub> may be covalently attached to A, and the conducting polymer comprises the structure:





wherein G, H, I, and J are aromatic groups, d = 1, 2, and  $d^1 = 0$ , 1, such that when  $d^1 = 0$ ,  $d^2 = 0$  and when  $d^1 = 1$ ,  $d^2 = 0$ , 1. In some embodiments, G and H may be the same or different, and each may be selected from the group consisting of:

In some embodiments, I and J may be the same or different and each is selected from the group consisting of:

In some embodiments, A may be selected from the group consisting of:

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wherein any hydrogen in A can be substituted by  $R^5$ ,  $R^5$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^6$ ,  $N(R^6)(R^7)$ ,  $C(O)N(R^6)(R^7)$ , F, Cl, Br,  $NO_2$ , CN, acyl, carboxylate, hydroxy;  $R^6$  and  $R^7$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;  $Z^1$  is selected from the group consisting of O, S and O and O and O are the same or different and each is selected from the group consisting of O, O0 alkyl, and O1 aryl; O2 alkyl, and O3 aryl; O3 and O4 aryl; O5 and O6 are the same or different and each is selected from the group consisting of:



wherein any hydrogen in B and D can be substituted by  $R^9$ ,  $R^9$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^{10}$ ,  $N(R^{10})(R^{11})$ ,  $C(O)N(R^{10})(R^{11})$ , F, Cl, Br,  $NO_2$ , CN, acyl, carboxylate, hydroxy,  $R^{10}$  and  $R^{11}$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl; C may be selected from the aromatic group consisting of:

wherein  $R^{12}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl and aryl; any hydrogen in C can be substituted by F which is represented by  $R^{13}$ ,  $R^{13}$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^{14}$ ,  $N(R^{14})(R^{15})$ ,  $C(O)N(R^{14})(R^{15})$ , F, Cl, Br, NO<sub>2</sub>, CN, acyl, carboxylate, hydroxy;  $R^{14}$  and  $R^{15}$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;  $Z^2$  is selected from the group consisting of O, S and  $NR^{16}$  and  $R^{16}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl.

In one set of embodiments, A may be selected from the group consisting of:

and both B and D may be:

In the Claims, column 28, line 36, please add the following:

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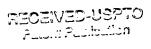
--5. The article of claim 1, wherein the conducting polymer is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.

- 6. The article of claim 1, wherein a portion of the conducting polymer comprises a multidentate ligand.
- 7. The article of claim 1, further comprising a metal ion bonded to a portion of the conducting polymer.
- 8. The article of claim 1, wherein the nanoscopic pathway comprises a pathway of nanoparticles.
- 9. The article of claim 8, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, semiconductor clusters, colloids and fibers.
- 10. The article of claim 9, wherein the nanotubes are selected from the group consisting of carbon nanotubes and metallized nanotubes.
- 11. The article of claim 9, wherein the colloids are selected from the group consisting of gold colloids and silver colloids.
- 12. The article of claim 9, wherein the colloids comprise colloidal aggregates.
- 13. The article of claim 9, wherein the fibers comprise graphite.
- 14. The article of claim 1, wherein the nanoscopic pathway comprises a biological species.

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15. The article of claim 14, wherein the biological species is selected from the group consisting of DNA and redox-active enzymes.

- 16. The article of claim 1, wherein the nanoscopic pathway includes a metal ion.
- 17. The article of claim 16, wherein the metal ion is selected from the group consisting of transition metals, lanthanides and actinides.
- 18. The article of claim 16, wherein the metal ion is selected from the group consisting of iron, copper, nickel, cobalt, ruthenium, iridium, manganese, chromium, molybdenum, vanadium, uranium.
- 19. The article of claim 1, wherein the dielectric is selected from the group consisting of a polymer, a ceramic, a solvent, a vacuum, a gas, a liquid crystal phase, a microphase-separated block copolymer structure and combinations thereof.
- 20. The article of claim 19, wherein the dielectric comprises a polymer.
- 21. The article of claim 20, wherein the dielectric polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.
- 22. The article of claim 20, wherein the dielectric polymer comprises a gel.
- 23. The article of claim 20, wherein the dielectric polymer is attached to the conducting polymer.



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24. The article of claim 23, wherein the dielectric polymer is attached to the conducting polymer via a chemical bond.

- 25. The article of claim 24, wherein the dielectric polymer is chemically bonded to the conducting polymer via a metal ion.
- 26. The article of claim 19, wherein the ceramic is selected from the group consisting of a metal oxide and a mixed metal oxide.
- 27. The article of claim 26, wherein the ceramic is a silicate.
- 28. The article of claim 27, wherein the silicate is a porous silicate.
- 29. The article of claim 1, wherein the dielectric comprises a biological species.
- 30. The article of claim 1, wherein the dielectric includes a metal ion.
- 31. The article of claim 1, wherein at least a portion of the nanoscopic pathway or the dielectric comprises a block co-polymer.
- 32. The article of claim 31, wherein the block co-polymer includes blocks comprising a dielectric.
- 33. The article of claim 32, wherein the dielectric is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.

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34. The article of claim 31, wherein the block co-polymer includes blocks comprising a conducting material.

- 35. The article of claim 34, wherein the blocks comprising a conducting material is selected from the group consisting of a conjugated organic group and nanoparticles.
- 36. The article of claim 35, wherein the conjugated organic group is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a carbon ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.
- 37. The article of claim 35, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, colloids, and fibers.
- 38. The article of claim 1, wherein the dielectric is non-conducting at a first electrochemical potential range and is capable of having a resistivity of less than 10<sup>-4</sup> times a resistivity at a second chemical potential.
- 39. The article of claim 1, wherein the nanoscopic switch is positioned in at least a portion of the dielectric.
- 40. The article of claim 1, wherein the nanoscopic switch is positioned in the nanoscopic pathway.
- 41. The article of claim 1, wherein the nanoscopic switch and the nanoscopic pathway are capable of being redox-matched.

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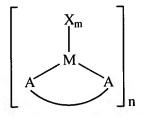
42. The article of claim 1, wherein the nanoscopic switch is redox-active.

- 43. The article of claim 1, wherein the nanoscopic switch is a metal ion.
- 44. The article of claim 1, wherein the nanoscopic switch comprises a biological species selected from the group consisting of DNA and a redox-active enzyme.
- 45. The article of claim 1, wherein the nanoscopic switch is attached to a portion of the conducting polymer.
- 46. The article of claim 1, wherein the nanoscopic switch is capable of being activated to alter the conductivity of the nanoscopic pathway.
- 47. The article of claim 46, wherein the nanoscopic switch is capable of altering the conductivity upon binding to an analyte.
- 48. The article of claim 1, wherein the nanoscopic pathway is a conductor within a first electrochemical potential range.
- 49. The article of claim 48, wherein the nanoscopic pathway is a first nanoscopic pathway, and the dielectric comprises a second nanoscopic pathway.
- 50. The article of claim 49, wherein the second pathway is a conductor within a second electrochemical potential range.
- 51. The article of claim 50, wherein the second electrochemical potential range is greater than the first electrochemical potential range.



52. The article of claim 49, wherein the second pathway is DNA.

- 53. The article of claim 1, wherein the nanoscopic pathway and the nanoscopic switch are redox-matched.
- 54. The article of claim 53, wherein the nanoscopic pathway and the nanoscopic switch are redox-matched within a defined electrochemical potential range.
- 55. The article of claim 16, wherein the nanoscopic pathway and metal ion are not redox-matched when the metal ion has a first ligand environment, and wherein the nanoscopic pathway and the metal ion are redox matched when the metal ion has a second ligand environment.
- 56. A sensor comprising the article of claim 1, for detecting the presence of an analyte.
- 57. The sensor of claim 56, wherein the nanoscopic switch is a detection site for the analyte.
- 58. The sensor of claim 57, wherein the sensor further comprises two electrodes positioned at either end of the nanoscopic pathway.
- 59. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric

structure comprising linkages through at least one atom in



and X are selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR1, —CO2C(R¹)<sub>3</sub>, —CONC(R¹)<sub>2</sub>, cyano, nitro, alkyloxy, aryloxy, hydroxyl, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR¹COR², thioalkyl, thioaryl,—SO<sub>2</sub>R¹, —SOR¹, —SO<sub>2</sub>OR¹, F, Cl, Br, and I; R¹ and R² can be the same or different, and each is selected from the group consisting of hydrogen, C1-C10 alkyl, C1-C10 heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0 - 3.

- 60. The article of claim 4, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.
- 61. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:

wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, and the polymeric structure comprises linkages through at least one of any R<sup>3</sup> - R<sup>6</sup> units or X and R<sup>3</sup> - R<sup>6</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>)<sub>3</sub>, —CONC(R<sup>1</sup>)<sub>2</sub>, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl,—SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, —SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, I, or where possible, any two R groups combining to form a ring structure; R<sup>1</sup>

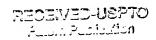
and  $R^2$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I; and X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO2C( $R^1$ )<sub>3</sub>, —CONC( $R^1$ )<sub>2</sub>, cyano, alkyloxy, aryloxy, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —  $NR^1COR^2$ , thioalkyl, thioaryl,— $SO_2R^1$ ,— $SOR^1$ ,— $SO_2OR^1$ , F, Cl, Br, and I;  $R^1$  and  $R^2$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and M = 0 - 3.

- 62. The article of claim 61, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.
- 63. The article of claim 61, wherein R3 or R6 comprises the formula:

64. The article of claim 61, wherein X comprises the formula:

comprises a species selected from the group consisting of a dielectric and a conductive nanoscopic pathway, and n is an integer greater than 0.

- 65. The article of claim 64, wherein the continuous chains of atoms comprises chains of methylene units optionally interrupted by an atom selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus.
- 66. The article of claim 64, wherein the continuous chains comprise chains of ethylene,
- 67. The article of claim 1, wherein X comprises the formula:



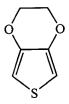
Patent No.: 7,186,355

68. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:

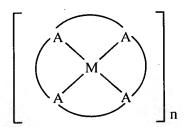
wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric structure comprising linkages through at least one atom in  $R^7 - R^{12}$  units, and  $R^7 - R^{12}$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C( $R^1$ )<sub>3</sub>, —CONC( $R^1$ )<sub>2</sub>, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —  $NR^1COR^2$ , thioalkyl, thioaryl,— $SO_2R^1$ ,— $SOR^1$ , —  $SO_2OR^1$ , F, Cl, Br, and I, or where possible, any two R groups combining to form a ring structure;  $R^1$  and  $R^2$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I.

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- 69. The article of claim 68, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.
- 70. The article of claim 68, wherein R<sup>10</sup> is:



71. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric

structure comprising linkages through at least one atom in , and any unit or X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>) 3, —CONC(R<sup>1</sup>) 2, cyano, nitro, alkyloxy, aryloxy, hydroxyl, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl,—SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, —SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, and I; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0-2.

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72. The article of claim 71, wherein the structure comprises a 1-, 2- or 3- dimensional array of n monomer units.

73. The article of claim 71, wherein the four units comprise a macrocycle.

74. The article of claim 73, wherein the macrocycle is selected from the group consisting of cyclams, phthalocyanines and porphyrins.

75. The article of claim 73, wherein the metal ion is a transition metal ion.—

This request does not involve correction of Applicant errors; accordingly no fee is required.

This Certificate of Correction implements the Amendment After Allowance Under 37 C.F.R. 1.312 filed on November 16, 2006. According to papers received by Applicant from the Patent Office, the Amendment After Allowance was "entered in part" by the Examiner. However, pursuant to correspondence with both the Examiner and the Examiner's Supervisor, it is believed that the Amendment After Allowance should have been entered fully, and that this Certificate of Correction is proper.

Transmitted herewith is a proposed Certificate of Correction effecting such amendment. Patentee respectfully solicits the granting of the requested Certificate of Correction.

Dated: January (8, 2008)

Respectfully submitted,

Timothy J. Oyer, Rh.D., Registration No.: 36,628 Karen V. Martin, Ph.D., Registration No.: 61,652

WOLF, GREENFIELD & SACKS, P.C.

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### UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

Page 1 of 22

PATENT NO.

7,186,355

APPLICATION NO.

09/777,725

ISSUE DATE

March 6, 2007

INVENTOR(S)

Timothy M. Swager

It is certified that an error appears or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Specification:

At column 1, line 10, please add the following:

-- Statement Regarding Federally Sponsored Research or Development

This invention was made with the support under the following government contract: N00014 -97-1-0174 awarded by the Office of Naval Research. The government has certain rights in the invention .--

At column 8, line 27, please add the following:

-- In some embodiments, an article of the present invention may comprise a nanoscopic pathway having a conductivity, an insulating dielectric surrounding the nanoscopic pathway, and a nanoscopic switch in electronic communication with the nanoscopic pathway being capable of altering the conductivity of the nanoscopic pathway. The nanoscopic pathway may comprise a conducting polymer, wherein the conducting polymer has a structure comprising the formula:

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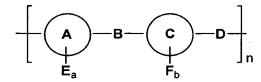
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ISSUE DATE

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INVENTOR(S)

Timothy M. Swager



wherein A and C are aromatic groups; B and D can be a heteroatom or metal and chosen from a group of N, P, S, As, Se, or -CC-M-CC-(M=FeLx, RuLx, PdLx, PtLx, CoLx, RhLx, where L is neutral (phosphine, nitrogen, or  $\pi$ -arene based ligand) or charged (nitrogen, oxygen, or charged  $\pi$ -arene ligand), or are selected from the group consisting of a carbon-carbon double bond and a carbon-carbon triple bond; and any hydrogen on aromatic group A and C can be replaced by E and F respectively, wherein a and b are integers which can be the same or different and a = 0 - 4, b = 0 - 4 such that when a = 0, b is nonzero and when b = 0, a is nonzero, and at least one of E and F includes a bicyclic ring system having aromatic or nonaromatic groups optionally interrupted by O, S, NR<sup>1</sup> and CR<sup>1</sup><sub>2</sub> wherein R<sup>1</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy and aryl and n is less than about 10,000, and wherein, when E or F is not said bicyclic ring system, E or F is a part of aromatic group A or C.

In some cases, Ea may be covalently attached to A, and the conducting polymer comprises the structure:

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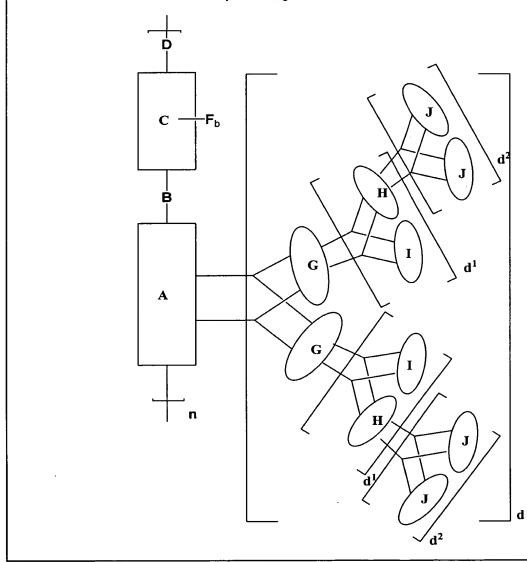
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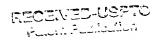
March 6, 2007

INVENTOR(S)

Timothy M. Swager



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INVENTOR(S)

Timothy M. Swager

wherein G, H, I, and J are aromatic groups, d = 1, 2, and  $d^1 = 0$ , 1, such that when  $d^1 = 0$ ,  $d^2 = 0$  and when  $d^1 = 1$ ,  $d^2 = 0$ , 1. In some embodiments, G and H may be the same or different, and each may be selected from the group consisting of:

$$\begin{cases} z^1 \\ z^1 \end{cases} \qquad \begin{cases} z^2 \\ z^2 \end{cases} \qquad z^2$$

In some embodiments, I and J may be the same or different and each is selected from the group consisting of:

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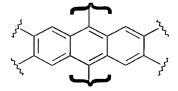
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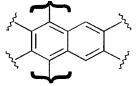
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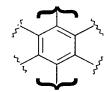
Timothy M. Swager

wherein any hydrogen in G, H, I and J can be substituted by R<sup>2</sup>, R<sup>2</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> alkoxy, phenoxy, C<sub>1</sub>-C<sub>20</sub> thioalkyl, thioaryl, C(O)OR<sup>3</sup>, N(R³)(R⁴), C(O)N(R³)(R⁴), F, Cl, Br, I, NO₂, CN, acyl, carboxylate, hydroxy, R³ and R⁴ can be the same or different and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, and aryl, Z<sup>1</sup> is selected from the group consisting of O, S and NR<sup>8</sup> wherein R<sup>8</sup> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, and aryl, and Z<sup>2</sup> is selected from the group consisting of F, Cl, OR3, SR3, NR3R4 and SiR8R3R4.

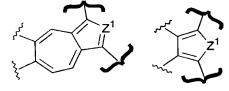
In some embodiments, A may be selected from the group consisting of:



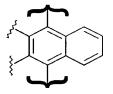


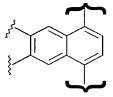












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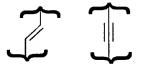
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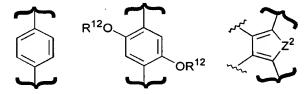
INVENTOR(S)

Timothy M. Swager

wherein any hydrogen in A can be substituted by R<sup>5</sup>, R<sup>5</sup> is selected from the group consisting of  $C_1-C_{20}$  alkyl, aryl,  $C_1-C_{20}$  alkoxy, phenoxy,  $C_1-C_{20}$  thioalkyl, thioaryl,  $C(O)OR^6$ ,  $N(R^6)(R^7)$ , C(O)N(R<sup>6</sup>)(R<sup>7</sup>), F, Cl, Br, NO<sub>2</sub>, CN, acyl, carboxylate, hydroxy; R<sup>6</sup> and R<sup>7</sup> can be the same or different and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, and aryl; Z<sup>1</sup> is selected from the group consisting of O, S and NR8 and R8 is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, and aryl; B and D can be the same or different and each is selected from the group consisting of:



wherein any hydrogen in B and D can be substituted by R9, R9 is selected from the group consisting of C<sub>1</sub>-C<sub>20</sub> alkyl, aryl, C<sub>1</sub>-C<sub>20</sub> alkoxy, phenoxy, C<sub>1</sub>-C<sub>20</sub> thioalkyl, thioaryl, C(O)OR<sup>10</sup>, N(R<sup>10</sup>)(R<sup>11</sup>), C(O)N(R<sup>10</sup>)(R<sup>11</sup>), F, Cl, Br, NO<sub>2</sub>, CN, acyl, carboxylate, hydroxy, R<sup>10</sup> and R<sup>11</sup> can be the same or different and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, and aryl; C may be selected from the aromatic group consisting of:



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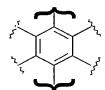
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INVENTOR(S)

Timothy M. Swager

wherein  $R^{12}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl and aryl; any hydrogen in C can be substituted by F which is represented by  $R^{13}$ ,  $R^{13}$  is selected from the group consisting of  $C_1$ - $C_{20}$  alkyl, aryl,  $C_1$ - $C_{20}$  alkoxy, phenoxy,  $C_1$ - $C_{20}$  thioalkyl, thioaryl,  $C(O)OR^{14}$ ,  $N(R^{14})(R^{15})$ ,  $C(O)N(R^{14})(R^{15})$ , F, Cl, Br, NO<sub>2</sub>, CN, acyl, carboxylate, hydroxy;  $R^{14}$  and  $R^{15}$  can be the same or different and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl;  $Z^2$  is selected from the group consisting of O, S and  $NR^{16}$  and  $R^{16}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{20}$  alkyl, and aryl.

In one set of embodiments, A may be selected from the group consisting of:





and both B and D may be:



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In the Claims, column 28, line 36, please add the following:

- --5. The article of claim 1, wherein the conducting polymer is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.
- 6. The article of claim 1, wherein a portion of the conducting polymer comprises a multi-dentate ligand.
- 7. The article of claim 1, further comprising a metal ion bonded to a portion of the conducting polymer.
- 8. The article of claim 1, wherein the nanoscopic pathway comprises a pathway of nanoparticles.
- 9. The article of claim 8, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, semiconductor clusters, colloids and fibers.
- 10. The article of claim 9, wherein the nanotubes are selected from the group consisting of carbon nanotubes and metallized nanotubes.

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- 11. The article of claim 9, wherein the colloids are selected from the group consisting of gold colloids and silver colloids.
- 12. The article of claim 9, wherein the colloids comprise colloidal aggregates.
- 13. The article of claim 9, wherein the fibers comprise graphite.
- 14. The article of claim 1, wherein the nanoscopic pathway comprises a biological species.
- 15. The article of claim 14, wherein the biological species is selected from the group consisting of DNA and redox-active enzymes.
- 16. The article of claim 1, wherein the nanoscopic pathway includes a metal ion.
- 17. The article of claim 16, wherein the metal ion is selected from the group consisting of transition metals, lanthanides and actinides.
- 18. The article of claim 16, wherein the metal ion is selected from the group consisting of iron, copper, nickel, cobalt, ruthenium, iridium, manganese, chromium, molybdenum, vanadium, uranium.

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- 20. The article of claim 19, wherein the dielectric comprises a polymer.
- 21. The article of claim 20, wherein the dielectric polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.
- 22. The article of claim 20, wherein the dielectric polymer comprises a gel.
- 23. The article of claim 20, wherein the dielectric polymer is attached to the conducting polymer.
- 24. The article of claim 23, wherein the dielectric polymer is attached to the conducting polymer via a chemical bond.
- 25. The article of claim 24, wherein the dielectric polymer is chemically bonded to the conducting polymer via a metal ion.
- 26. The article of claim 19, wherein the ceramic is selected from the group consisting of a metal oxide and a mixed metal oxide.
- 27. The article of claim 26, wherein the ceramic is a silicate.

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- 28. The article of claim 27, wherein the silicate is a porous silicate.
- 29. The article of claim 1, wherein the dielectric comprises a biological species.
- 30. The article of claim 1, wherein the dielectric includes a metal ion.
- 31. The article of claim 1, wherein at least a portion of the nanoscopic pathway or the dielectric comprises a block co-polymer.
- 32. The article of claim 31, wherein the block co-polymer includes blocks comprising a dielectric.
- 33. The article of claim 32, wherein the dielectric is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.
- 34. The article of claim 31, wherein the block co-polymer includes blocks comprising a conducting material.
- 35. The article of claim 34, wherein the blocks comprising a conducting material is selected from the group consisting of a conjugated organic group and nanoparticles.

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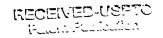
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Timothy M. Swager

- 36. The article of claim 35, wherein the conjugated organic group is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a carbon ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.
- 37. The article of claim 35, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, colloids, and fibers.
- 38. The article of claim 1, wherein the dielectric is non-conducting at a first electrochemical potential range and is capable of having a resistivity of less than 10<sup>-4</sup> times a resistivity at a second chemical potential.
- 39. The article of claim 1, wherein the nanoscopic switch is positioned in at least a portion of the dielectric.
- 40. The article of claim 1, wherein the nanoscopic switch is positioned in the nanoscopic pathway.
- 41. The article of claim 1, wherein the nanoscopic switch and the nanoscopic pathway are capable of being redox-matched.

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- 42. The article of claim 1, wherein the nanoscopic switch is redox-active.
- 43. The article of claim 1, wherein the nanoscopic switch is a metal ion.
- 44. The article of claim 1, wherein the nanoscopic switch comprises a biological species selected from the group consisting of DNA and a redox-active enzyme.
- 45. The article of claim 1, wherein the nanoscopic switch is attached to a portion of the conducting polymer.
- 46. The article of claim 1, wherein the nanoscopic switch is capable of being activated to alter the conductivity of the nanoscopic pathway.
- 47. The article of claim 46, wherein the nanoscopic switch is capable of altering the conductivity upon binding to an analyte.
- 48. The article of claim 1, wherein the nanoscopic pathway is a conductor within a first electrochemical potential range.
- 49. The article of claim 48, wherein the nanoscopic pathway is a first nanoscopic pathway, and the dielectric comprises a second nanoscopic pathway.

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- 50. The article of claim 49, wherein the second pathway is a conductor within a second electrochemical potential range.
- 51. The article of claim 50, wherein the second electrochemical potential range is greater than: the first electrochemical potential range.
- 52. The article of claim 49, wherein the second pathway is DNA.
- 53. The article of claim 1, wherein the nanoscopic pathway and the nanoscopic switch are redoxmatched.
- 54. The article of claim 53, wherein the nanoscopic pathway and the nanoscopic switch are redox-matched within a defined electrochemical potential range.
- 55. The article of claim 16, wherein the nanoscopic pathway and metal ion are not redoxmatched when the metal ion has a first ligand environment, and wherein the nanoscopic pathway and the metal ion are redox matched when the metal ion has a second ligand environment.
- 56. A sensor comprising the article of claim 1, for detecting the presence of an analyte.
- 57. The sensor of claim 56, wherein the nanoscopic switch is a detection site for the analyte.

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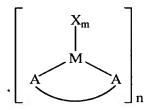
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INVENTOR(S)

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58. The sensor of claim 57, wherein the sensor further comprises two electrodes positioned at either end of the nanoscopic pathway.

59. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric

structure comprising linkages through at least one atom in



and X are selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR1, —CO2C(R¹)<sub>3</sub>, —CONC(R¹)<sub>2</sub>, cyano, nitro, alkyloxy, aryloxy, hydroxyl, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR¹COR², thioalkyl, thioaryl,—SO₂R¹, —SOR¹, — SO₂OR¹, F, Cl, Br, and I; R¹ and R² can be the same or different, and each is selected from the group consisting of hydrogen, C1-C10 alkyl, C1-C10 heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl,

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Br, and I, and m = 0 - 3.

60. The article of claim 4, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.

61. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:

wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, and the polymeric structure comprises linkages through at least one of any  $R^3$  -  $R^6$  units or X and  $R^3$  -  $R^6$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C( $R^1$ )<sub>3</sub>, —CONC( $R^1$ )<sub>2</sub>, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl,—SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, — SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, I, or where possible, any two R groups combining to form a ring structure;  $R^1$ 

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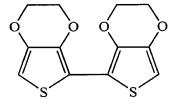
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INVENTOR(S)

Timothy M. Swager

and  $R^2$  can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I; and X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO2C(R<sup>1</sup>)<sub>3</sub>, —CONC(R<sup>1</sup>)<sub>2</sub>, cyano, alkyloxy, aryloxy, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl,—SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, —SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, and I; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen,  $C_1$ - $C_{10}$  alkyl,  $C_1$ - $C_{10}$  heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0 - 3.

- 62. The article of claim 61, wherein the structure comprises a 1-, 2- or 3-dimensional array of nonomer units.
- 63. The article of claim 61, wherein R3 or R6 comprises the formula:



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7,186,355

APPLICATION NO.

09/777,725

**ISSUE DATE** 

March 6, 2007

INVENTOR(S)

Timothy M. Swager

64. The article of claim 61, wherein X comprises the formula:

comprises two continuous chains of atoms and

comprises a species selected from the group consisting of a dielectric and a conductive

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March 6, 2007

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nanoscopic pathway, and n is an integer greater than 0.

- 65. The article of claim 64, wherein the continuous chains of atoms comprises chains of methylene units optionally interrupted by an atom selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus.
- 66. The article of claim 64, wherein the continuous chains comprise chains of ethylene.
- 67. The article of claim 1, wherein X comprises the formula:

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68. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:

wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric structure comprising linkages through at least one atom in  $R^7 - R^{12}$  units, and R7 - R12 can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, — COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>)<sub>3</sub>, —CONC(R<sup>1</sup>)<sub>2</sub>, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, — NR1COR2, thioalkyl, thioaryl,—SO2R1, —SOR1, — SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, and I, or where possible, any two R groups combining to form a ring structure; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I.

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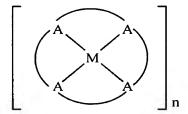
March 6, 2007

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- 69. The article of claim 68, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.
- 70. The article of claim 68, wherein R<sup>10</sup> is:

71. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric

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monomer units.

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structure comprising linkages through at least one atom in



unit or X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR<sup>1</sup>, —CO<sub>2</sub>C(R<sup>1</sup>) 3, —CONC(R1) 2, cyano, nitro, alkyloxy, aryloxy, hydroxyl, hydroxyalkyl, amino, alkylamino,

dialkylamino, arylamino, diarylamino, — NR<sup>1</sup>COR<sup>2</sup>, thioalkyl, thioaryl,—SO<sub>2</sub>R<sup>1</sup>, —SOR<sup>1</sup>, — SO<sub>2</sub>OR<sup>1</sup>, F, Cl, Br, and I; R<sup>1</sup> and R<sup>2</sup> can be the same or different, and each is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0-2.

72. The article of claim 71, wherein the structure comprises a 1-, 2- or 3- dimensional array of n

73. The article of claim 71, wherein the four



units comprise a macrocycle.

- 74. The article of claim 73, wherein the macrocycle is selected from the group consisting of cyclams, phthalocyanines and porphyrins.
- 75. The article of claim 73, wherein the metal ion is a transition metal ion.--